

THE CATHODIC PRECIPITATION OF CARBON.

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(CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.)

Some years ago¹ one of us (S) called attention to the electrolytic precipitation of iron, by the current, from citrate and tartrate solutions. In doing so, mention was made that on dissolving the deposited metal "in dilute, cold sulphuric acid a strong odor of hydrocarbons was perceptible." Later,² reference was again made to this fact and conditions given, observing which, the contamination of the metal by carbon might be avoided. In electro-analysis, the question of the contamination of metals by carbon, if the metals have been precipitated from organic electrolytes, has been quite freely discussed. However, the contamination in nearly all instances has been regarded as a result of carelessness in manipulation and may be avoided.

During the past summer we made observations, on the conduct of certain organic acids under the influence of the current, which seem of value, hence a brief account of them is submitted in this communication.

To begin, it was tried to ascertain the degree of reduction of oxalic acid at the cathode. The gasometric method was called into use, *e. g.*, a comparison of the volume of hydrogen evolved in the cell, with that liberated in a voltameter in the same period. It soon became evident that this procedure would not be delicate enough to detect any such reduction. However, while occupied in this way with an ammoniacal tartrate solution, a black deposit made its appearance on the cathode. When held in the flame it burned off completely from the platinum plate. The latter had an area of 100 sq. cm. Several actual trials may be here introduced. Thirty-seven

¹ *Am. Chem. Jr.*, 10, 330 and *Jr. Analyt. and Applied Chemistry*, 5, 488.

² Smith's "Electrochemical Analysis," 3d edition, p. 100.

and one-half grams of tartaric acid were dissolved in water, neutralized one-half with ammonia, then diluted to a liter. Portions of this solution were electrolyzed at a temperature of 60° C. The anode was a platinum spiral suspended in a porous cup. The cathode was the foil to which reference has been made. A current of one ampere and twelve and one-half volts acted for a period of two hours. A black deposit showed itself on the cathode. It burned off in the flame. In another experiment, with conditions like those just mentioned, discarding, however, the cup, there was no deposit on the cathode, but the solution was deep yellow in color. Again, in electrolyzing a portion of the ammonium tartrate without the porous cup, but surrounding the anode with a muslin bag, at the ordinary temperature, with a current of 4 amperes and 6 volts, there was a very considerable deposit, black in color, on the cathode. It burned away, with the exception of a mere iridescence, when held in a flame. In another experiment, fifteen grams of tartaric acid were neutralized with ammonia, diluted to 150 c.c. and electrolyzed at 60° C., for four hours, with a current of 4 amperes and 6 volts. The anode and cathode had both been weighed. The cathode became coated with a grayish black deposit. The anode sustained a loss in weight and only one-third of the cathodic deposit was carbon, the remainder being platinum, which had come from the anode.

Upon substituting a solution of citric acid (70 grams to the liter) and electrolyzing at 70° C., for three hours, with a current of one ampere and sixteen volts, a heavy black deposit separated on the cathode. It was not affected by hydrochloric acid. It burned away completely in a Bunsen flame. The electrodes were separated by a porous cup. In other experiments a muslin bag surrounded the anode. This bag had previously been well soaked in caustic soda. The usual black cathodic deposit was obtained. It burned away completely on heating. On digesting this deposit with chromic acid, carbon dioxide was obtained and recognized by its reaction with lime water.

Another trial is worthy of notice. In it a half normal solution of ammonium citrate, made alkaline with ammonia, was electrolyzed for a period of five hours with a current of 4 amperes and 6 volts. The anode was protected by a muslin bag. The solution

rapidly took on a yellow color, a distinct odor of acetamide was evolved and a black deposit appeared upon the cathode. It both burned on heating and generated carbon dioxide with a chromic acid mixture. It may be added that the solution was not heated from without as it developed a great deal of heat during the passage of the current.

Similar results were obtained on electrolyzing a like solution with out a diaphragm.

Other experiments were as follows:

1. Five grams of sodium citrate and one gram of citric acid were dissolved in 150 c.c. of water and electrolyzed at 60° C., for five hours, with a current of 4 amperes and 11 volts. There was a brass-like deposit on the cathode. It weighed 0.0018 gram, while the anode had lost 0.0014 gram.

2. Fifteen grams of citric acid, neutralized with ammonia and diluted to 150 c.c., were electrolyzed at 60° C., for four hours, with a current of 4 amperes and 6 volts. A grayish black deposit separated on the cathode. It equaled 0.0014 gram, which represents carbon. The anode lost in all 0.0103 gram in weight.

In the many trials made, the solutions gradually acquired first a pale yellow color which in turn passed to brown and at times almost black without becoming turbid. However, it must be said that solutions of ammonium oxalate, ammonium formate, ammonium acetate and ammonium succinate did not yield black deposits to the cathode. In solutions of ammonium lactate and benzoate they appeared as readily as in tartrate and citrate solutions.

This deposition of carbon upon the cathode is extremely interesting. In 1896, Coehn (*Z. f. Elektrochemie* (1896), p. 541) called attention to the fact that when carbon was made an anode in the electrolysis of sulphuric acid, the latter became at first yellow, and by prolonging the experiment, dark red and reddish brown in color. If this meant a solution of carbon the latter must presumably be in the form of ions, *e. g.*, in a form directable by the current. It must be in a form, which, as it does not decompose water, would appear at the anode. With these thoughts before him, Coehn electrolyzed sulphuric acid of varying concentration with an anode of carbon and a cathode of platinum. The result was a splendid deposition of carbon on the cathode. It burned away completely on

heating and gave carbon dioxide when acted upon with a chromic acid mixture. In later experiments, Coehn was able to determine, in the electrolytic way, the equivalent of carbon and found it to be 3.

Turning to our observations with tartaric and citric acid, it must be that these are broken down at the anode, during electrolysis; that the carbon thus liberated from combination in these acids enters aqueous solution as a hydrate of which the carbon is cation, and this, under influence of the current, passes in its ionic form to the cathode just as a metal, in some salt, does under similar influence. When, therefore, iron is deposited from a citrate or tartrate electrolyte, the carbon ions wander with the iron ions to the cathode, and there an alloy of iron and carbon appears. This alloy, on treatment with dilute sulphuric acid, generates hydrocarbons. Very little, if any, of the carbon deposited with iron is graphitic. It is chemically combined. Just as zinc and copper, from certain electrolytes, separate as brass, so do the carbon and iron separate as an alloy from the electrolytes which have been under discussion.

The conclusions warranted from the experiments here noticed and many others like them are:

1. Carbon is deposited on the cathode from solutions containing tartaric, citric, lactic and benzoic acids. This is particularly the case if a stationary anode be used along with high current density.

2. From solutions like those in 1, where high current density is employed, platinum will dissolve from the anode and be precipitated in part upon the cathode.

UNIVERSITY OF PENNSYLVANIA.

Stated Meeting January 18, 1907.

President SMITH in the Chair.

The following papers were read:

"Pennsylvania at the Jamestown Exposition, illustrated by the Lincoln Migration," by PROF. MARION D. LEARNED, which was discussed by Mr. Richard Wood, Prof. Cheyney and Prof. Leslie W. Miller.

"Reproduction, Animal Life Cycles and the Biological Unit," by PROF. THOMAS H. MONTGOMERY.